

FORM PTC-1390 (REV 5-93)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			1066-99
INTERNATIONAL APPLICATION NO. PCT/GB98/01597		INTERNATIONAL FILING DATE 1 June 1998	U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>09/424811</b>
TITLE OF INVENTION METHOD OF PRODUCING WATER-SOLUBLE GLASS FIBRES		PRIORITY DATE CLAIMED 31 May 1997	
APPLICANT(S) FOR DO/EO/US THOMAS GILCHRIST; DAVID MICHAEL HEALY			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li><input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <li><input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li><input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li> <li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li><input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <li><input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li><input type="checkbox"/> have been transmitted by the International Bureau.</li> <li><input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li><input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li><input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li><input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol>			
Items 11. to 16. below concern other document(s) or information included:			
<ol style="list-style-type: none"> <li><input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li><input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification.</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input type="checkbox"/> Other items or information:</li> </ol>			

66067-113099

U.S. APPLICATION NO. (if known) 37 CFR 1.50 <b>097424811</b>		INTERNATIONAL APPLICATION NO. PCT/GB98/01597		ATTORNEY'S DOCKET NUMBER 1066-99	
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17. ☒ The following fees are submitted:

**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**  
 Search Report has been prepared by the EPO or JPO.....EPO.....

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
 .....  
 No international preliminary examination fee paid to USPTO (37 CFR 1.482)  
 but international search fee paid to USPTO (37 CFR 1.445(a)(2))..

Neither international preliminary examination fee (37 CFR 1.482) nor  
 international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
 and all claims satisfied provisions of PCT Article 33(2)-(4).....

				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 840.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 130.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	20 -20 -	0	X	\$ -0-	
Independent Claims	1 -3 -	0	X	\$ -0-	
Multiple dependent claims(s) (if applicable)			+	\$ -0-	
<b>TOTAL OF ABOVE CALCULATIONS</b> =				\$ 970.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$ 485.00	-
<b>SUBTOTAL</b> =				\$ 485.00	
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ -0-	
<b>TOTAL NATIONAL FEE</b> =				\$ 485.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 40.00	
<b>TOTAL FEES ENCLOSED</b> =				\$ 525.00	
				Amount to be:	
				refunded \$	
				charged \$	

a. ☒ A check in the amount of \$ 525.00 to cover the above fees is enclosed.

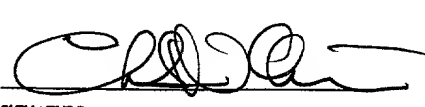
b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 04-1406. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

CHARLES N. QUINN, ESQUIRE  
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 1601 Market Street, Suite 720  
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 SIGNATURE  
 CHARLES N. QUINN  
 NAME  
 27,223  
 REGISTRATION NUMBER

660677-11342450

Applicant or Patentee: Thomas Gilchrist; David Michael Healy Attorney Docket No 1066-99  
Serial or Patent No: \_\_\_\_\_  
Filed or Issued: 30 November 1999  
For: "Method of Producing Water-Soluble Glass Fibres"

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS  
(37 CFR 1.9(f) AND 1.27(c) - SMALL BUSINESS CONCERN)**

I hereby declare that I am

☐ the owner of the small business concern identified below:  
☒ the official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN Giltech Limited  
ADDRESS OF CONCERN 12 North Harbour Estate, Ayr, KA8 8AA, United Kingdom

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.1-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the above-identified invention by inventor Thomas Gilchrist and David Michael Healy described in

☒ the Specification filed herewith  
☐ Application S.N. \_\_\_\_\_, filed \_\_\_\_\_  
☐ Patent No. \_\_\_\_\_, filed \_\_\_\_\_ and issued \_\_\_\_\_

If the rights held by the small business concern are not exclusive, each individual concern or organization having rights to the invention is listed below\* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

\*NOTE Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities (37 CFR 1.27)

FULL NAME \_\_\_\_\_  
ADDRESS \_\_\_\_\_

☐ INDIVIDUAL ☐ SMALL BUSINESS ☐ NON-PROFIT ORGANIZATION

FULL NAME \_\_\_\_\_  
ADDRESS \_\_\_\_\_

☐ INDIVIDUAL ☐ SMALL BUSINESS ☐ NON-PROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING THOMAS GILCHRIST  
TITLE OF ORGANIZATION GILTECH LTD  
ADDRESS OF PERSON SIGNING 61 HILTON ROAD Ayr KAT 2TW

SIGNATURE Thomas Gilchrist DATE 15 November 1999

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420 Rec'd PCT/PTO 30 NOV 1999

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s) : Thomas Gilchrist; David Michael Healy  
Int'l Application No. : PCT/GB98/01597  
Application No. : Not yet assigned  
Filed : 30 November 1999  
Title : METHOD OF PRODUCING WATER-SOLUBLE GLASS FIBRES

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Suite 720, 1601 Market Street  
Philadelphia, Pa. 19103  
215-563-4100  
215-563-4044 (fax)  
Docket No.: 1066-99  
Dated: 30 November 1999

ASST. COMMISSIONER FOR PATENTS  
Box PCT  
WASHINGTON, DC 20231


Dear Sir:

PRELIMINARY AMENDMENT

Prior to computation of the filing fee and prior to examination of the application, please amend certain of the claims as set forth in Attachment 1 and add new claims 11 through 20 to the application as set forth in Attachment 2.

By entry of this preliminary amendment, a prompt and thorough examination of this application on the merits is solicited.

Respectfully submitted,



Charles N. Quinn  
Reg. No. 27,223  
Attorney for Applicant

CNQ:jmn  
Enclosures

**DEB**

By: \_\_\_\_\_

Charles N. Quinn  
November 30, 1999

## ATTACHMENT 1

3. (Amended) A method as claimed in [either one of Claims] Claim 1 [and 2] wherein said working temperature is 50-300°C above the Tg of the glass.
4. (Amended) A method as claimed in [either one of Claims] Claim 1 [and 2] wherein said working temperature is at least 200°C below the temperature to which the glass is initially heated.
5. (Amended) A method as claimed in [any one of Claims] Claim 1 [to 4] wherein glass wool is formed.
6. (Amended) A method as claimed in [any one of Claims] Claim 1 [to 5] wherein phosphorous pentoxide is used as the glass former.
7. (Amended) A method as claimed in [any one of] Claim 6 wherein boron containing compounds are used as glass modifiers.
9. (Amended) A method as claimed in [any one of Claims] Claim 1 [to 8] wherein said glass is a silver-ion releasing glass.

## ATTACHMENT 2

11. A method as claimed in Claim 2 wherein said working temperature is 50-300°C above the Tg of the glass.
12. A method as claimed in Claim 2 wherein said working temperature is at least 200°C below the temperature to which the glass is initially heated.
13. A method as claimed in Claim 4 wherein glass wool is formed.
14. A method as claimed in Claim 5 wherein phosphorous pentoxide is used as the glass former.
15. A method as claimed in Claim 1 wherein boron containing compounds are used as glass modifiers.
16. A method as claimed in Claim 8 wherein said glass is a silver-ion releasing glass.
17. A method as claimed in Claim 7 wherein said glass is a silver-ion releasing glass.
18. A method as claimed in Claim 5 wherein said glass is a silver-ion releasing glass.

19. A method as claimed in Claim 4 wherein said glass is a silver-ion releasing glass.

20. A method as claimed in Claim 3 wherein said glass is a silver-ion releasing glass.

**Discussion**



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1 "Method of Producing Water-Soluble Glass Fibres"

2

3 The present invention relates to a method for the  
4 production of water soluble glass fibres and glass  
5 wool.

6

7 It is known that certain glasses, in which the usual  
8 glass former, silicon dioxide, is replaced with  
9 phosphorous pentoxide, are soluble in water and body  
10 fluids. The rate of dissolution is controlled largely  
11 by the addition of glass modifiers such as calcium  
12 oxide. In simple terms, the greater the concentration  
13 of the modifier the slower the rate of dissolution.  
14 The rate of dissolution may range from minutes through  
15 to several years.

16

17 Soluble phosphate based glasses which have demonstrated  
18 good biocompatibility can incorporate inorganic metals  
19 such that a sustained release of the metals can be  
20 provided at the wound site. Such materials can also  
21 find use in mechanical applications where, for example,  
22 slow release of an anti-corrosion agent may be  
23 beneficial.

24

25 Certain applications require that the glass is in the

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1 form of wool or fibres for mechanical applications such  
2 as insulation wool and packaging. Thus, for example,  
3 Mohr et al in "Fibre Glass" (Van Norstrand, Reinhold  
4 Company, New York 1978) and Jaray in "A New Method of  
5 Spinning Glass Fibres" (28th Annual SPI RP/C Institute  
6 proceedings 1973, Section 3-A) describe the production  
7 of wool and fibres, respectively, from molten glass.  
8 The glass fibres can be used for insulation,  
9 construction or even communication purposes. Glass  
10 wool also finds uses in packaging and insulation  
11 applications.

12  
13 Normally, glass fibres are produced from molten glass  
14 using traditional fibre pulling techniques; whereby  
15 filaments of high temperature molten glass (850°-  
16 1300°C) are formed into strands and stretched over pull  
17 rolls before being collected onto a reel.

18  
19 Glass wool formation is similar in that the glass is  
20 initially melted in a crucible. The crucible has  
21 suitable apertures to allow filaments of glass to flow  
22 downwards, which are then "blown" into wool using jets  
23 of either steam or compressed air. Alternatively,  
24 glass wool can be formed using a flame attenuation  
25 process, developed by Owens-Corning Fibreglass  
26 Corporation circa 1940. In this process molten glass  
27 passes through a bushing stage where primary filaments  
28 approximately 1 mm wide are formed. The fibres are  
29 then aligned into an exact uniformly juxtaposed array,  
30 using a fibre guide, into a jet flame issuing from an  
31 internal combustion burner. The jet flame causes  
32 thinning and lengthening of the fibres before they are  
33 collected on a steel mesh belt.

34  
35 In both cases, the glass is either supplied in molten  
36 form direct from a crucible or from a temperature-

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1 gradient furnace.

2

3 Generally, water soluble glasses do not lend themselves  
4 to these traditional fibre and wool forming techniques.

5 As an example, US Patent 4,604,097 of Graves et al  
6 discloses a water soluble drawn fibre, composed  
7 primarily of calcium oxide and phosphorous pentoxide.

8 The fibre produced has a very low tensile strength,  
9 compared to fibres spun from non-soluble glass  
10 compositions.

11

12 Further, water soluble glasses can also be chemically  
13 aggressive when molten, unlike traditional glasses  
14 where silicon dioxide is used as the glass former.  
15 Additionally, the fibres produced are prone to thermal  
16 shock and can suffer from devitrification or  
17 crystallisation.

18

19 To combat problems of devitrification and  
20 crystallisation, water soluble glass fibres have been  
21 previously produced in exacting conditions. Thus, for  
22 example, Zimmer et al in WO92/07801 discloses drawing  
23 fibres from a water soluble glass composed primarily of  
24 phosphorus pentoxide, calcium oxide and iron oxide. In  
25 order to keep the viscosity of the glass suitable for  
26 drawing, the fibres were drawn at 1200°C. Also as a  
27 result of the chemically aggressive nature of the glass  
28 at that temperature the glass was pulled in an oxygen  
29 rich atmosphere (as high as 80% oxygen by volume).  
30 Obviously the commercial production of glass fibres  
31 under these high temperature controlled atmospheric  
32 conditions is expensive.

33

34 The problems of working with water soluble glass are  
35 compounded by the very nature of the glass. Metal  
36 oxides of elements such as lead and tellurium have

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1 previously been used in glass as additives to affect  
2 qualities of the glass; crystallisation temperature,  
3 viscosity and density, for example. As a result of  
4 environmental concerns and particularly when the  
5 glasses are to be used in a biological application  
6 these additives must be avoided and replaced by more  
7 acceptable alternatives.

8  
9 Therefore, it is an object of the present invention to  
10 provide environmentally acceptable water soluble glass  
11 fibres with suitable mechanical properties, and to  
12 produce said fibres under less forcing conditions.

13  
14 The present invention provides a method for forming a  
15 water-soluble glass fibre and/or glass wool, the method  
16 comprising producing a water-soluble glass and heating  
17 said glass above its melting point to form molten  
18 glass, cooling at least a portion of said molten glass  
19 to a pre-selected working temperature and then  
20 processing said molten glass having said working  
21 temperature into fibres and/or wool.

22  
23 Generally, the glass is initially heated to a melting  
24 temperature of 500°-1200°C, preferably 750°-1050°C.  
25 The temperature is then slowly lowered to the working  
26 temperature at which fibre formation occurs.

27  
28 Generally, the working temperature of the glass will be  
29 at least 200°C lower than the temperature at which the  
30 glass is initially heated. Suitable working  
31 temperatures may fall within the following ranges 400°-  
32 500°C, 500°-900°C (preferably 550°-700°C, more  
33 preferably 550°-650°C, especially 600°-650°C) and 800-  
34 1000°C. The working temperature selected will depend  
35 upon the glass composition, but an approximate  
36 indication of a suitable working temperature can be

1 established as hereinafter described. Depending upon  
2 the glass composition used, the working temperature may  
3 be a range of suitable temperatures. The range of  
4 working temperatures may be narrow, for example of only  
5 10°C, so that fibre formation may occur only between  
6 the temperature of N°C to (N+10)°C. Other glass  
7 compositions may have a wider temperature range for the  
8 working temperature in which glass formation is  
9 possible.

10

11 Alternatively, the working temperature of the glass may  
12 be defined as 50-300°C above the Tg of the glass.

13

14 In order to obtain an approximate indication of the  
15 working temperature for any particular glass  
16 composition, the glass composition should be slowly  
17 heated to its melting point. As soon as the glass is  
18 molten, frequent attempts to pull the composition  
19 upwardly to form a fibre should be made, with the  
20 temperature of the composition being very gradually  
21 increased between attempts. The temperature range of  
22 the composition during which fibre formation is  
23 possible should be noted and used as a preliminary  
24 working temperature in the process of the invention.

25

26 It will be clear to those skilled in the art that the  
27 pulling speed at which the fibre is drawn off can  
28 affect the choice of working temperature and the  
29 diameter of the fibre required. Where a fibre of  
30 relatively large diameter is required, the fibre tends  
31 to be pulled more slowly and the working temperature  
32 may need to be decreased slightly. Where a fibre of  
33 relatively small diameter is required (eg a glass  
34 wool), the fibres may be drawn at the much higher  
35 pulling speed and the working temperature may need to  
36 be increased (thus lowering the viscosity of the

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1 composition to accommodate the increased pulling  
2 speed). Selection of the exact working temperature in  
3 respect of any particular fibre size and composition  
4 will be a simple matter of routine evaluation of  
5 optimal process conditions.

6  
7 With reference to the "working temperature" of the  
8 glass, the skilled person will appreciate that the  
9 furnace temperature may differ considerably from the  
10 temperature of the glass itself and indeed there may be  
11 a significant temperature gradient in the glass.  
12 Ideally the "working temperature" will be the  
13 temperature of the glass as fibre formation (ie.  
14 pulling) takes place. In many compositions however, it  
15 may not be practical to measure the temperature at the  
16 surface of the glass where pulling occurs by insertion  
17 of a temperature probe as the introduction of the probe  
18 may precipitate crystallisation of the glass. One  
19 alternative is to place a temperature probe into the  
20 bushing and to monitor the bushing temperature which  
21 will be a good indicator of the glass temperature at  
22 the moment of fibre formation. Alternatively an Infra  
23 Red pyrometer may be focused onto the appropriate area  
24 of the glass and used to monitor the temperature.

25  
26 The glass to be formed into fibres will generally be  
27 heated until molten, optionally clarified, and then  
28 cooled slowly and controllably until the appropriate  
29 working temperature is reached and fibre formation can  
30 commence. The initial heating of the glass above its  
31 melting point and the subsequent fibre formation may be  
32 carried out in a single vessel or, alternatively, the  
33 molten glass may be transferred to a vessel designed  
34 specifically for fibre formation. One way of holding  
35 the molten glass in a vessel having a bushing within  
36 its lower surface until the temperature drops to the

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1 required working temperature is to coat or fill the  
2 holes of the bushing with a material that gradually  
3 melts over the period of time taken for the glass to  
4 reach the temperature required.

5  
6 The most important aspect of the present invention is  
7 the manner in which the working temperature is reached.  
8 We have found that the molten glass, which may  
9 preferably be heated significantly above its melting  
10 point, should be allowed to cool in a highly controlled  
11 manner, the temperature being only gradually reduced  
12 until the working temperature is reached. A stirrer  
13 may be present to ensure that the temperature of the  
14 whole of the molten glass is kept as uniform as  
15 possible.

16  
17 The glass is cooled to a temperature at which the glass  
18 will not crystallise for at least the period of time  
19 needed to convert the melt to fibre. This temperature  
20 is termed a "holding temperature". The rate of cooling  
21 from this holding temperature is determined by the rate  
22 at which the melt is consumed at the bushing and the  
23 difference in temperature between the bushing  
24 temperature (the working temperature) and the melt  
25 holding temperature.

26  
27 Due to low viscosity and narrow temperature band for  
28 many of these compositions, control of the balance  
29 between melt temperature, bushing temperature and glass  
30 throughput rate is critical.

31  
32 According to a further aspect of the present invention  
33 there is provided a composition suitable for processing  
34 into glass fibres and/or wool.

35  
36 Phosphorous pentoxide ( $P_2O_5$ ) is preferably used as the

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1 glass former.

2

3 Generally the mole percentage of phosphorous pentoxide  
4 in the glass composition is less than 85%, preferably  
5 less than 60% and especially between 30-60%.

6

7 Alkali metals, alkaline earth metals and lanthanoid  
8 oxides or carbonates are preferably used as glass  
9 modifiers.

10

11 Generally, the mole percentage of alkali metals,  
12 alkaline earth metals and lanthanoid oxides or  
13 carbonates is less than 60%, preferably between 40-60%.

14

15 Boron containing compounds (eg  $B_2O_3$ ) are preferably used  
16 as glass additives.

17

18 Generally, the mole percentage of boron containing  
19 compounds is less than 15% or less, preferably less  
20 than 5%.

21

22 Other compounds may also be added to the glass to  
23 modify its properties, for example  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SO}_3$ ,  
24 sulphate ions ( $\text{SO}_4^{2-}$ ) or transition metal compounds (eg.  
25 first row transition metal compounds).

26

27 Typically the soluble glasses used in this invention  
28 comprise phosphorus pentoxide ( $P_2O_5$ ) as the principal  
29 glass-former, together with any one or more  
30 glass-modifying non-toxic materials such as sodium  
31 oxide ( $Na_2O$ ), potassium oxide ( $K_2O$ ), magnesium oxide  
32 ( $MgO$ ), zinc oxide ( $ZnO$ ) and calcium oxide ( $CaO$ ). The  
33 rate at which the glass dissolves in fluids is  
34 determined by the glass composition, generally by the  
35 ratio of glass-modifier to glass-former and by the  
36 relative proportions of the glass-modifiers in the



1 glass. By suitable adjustment of the glass  
2 composition, the dissolution rates in water at 38°C  
3 ranging from substantially zero to 25mg/cm<sup>2</sup>/hour or more  
4 can be designed. However, the most desirable  
5 dissolution rate R of the glass is between 0.01 and  
6 2.0mg/cm<sup>2</sup>/hour.

7  
8 The water-soluble glass is preferably a phosphate  
9 glass, and preferably comprises a source of silver ions  
10 which may advantageously be introduced during  
11 manufacture as silver orthophosphate (Ag<sub>3</sub>PO<sub>4</sub>). The  
12 glass preferably enables controlled release of silver  
13 and other constituents in the glass and the content of  
14 these additives can vary in accordance with conditions  
15 of use and desired rates of release, the content of  
16 silver generally being up to 5 mole %. While we are  
17 following convention in describing the composition of  
18 the glass in terms of the mole % of oxides, of halides  
19 and of sulphate ions, this is not intended to imply  
20 that such chemical species are present in the glass nor  
21 that they are used for the batch for the preparation of  
22 the glass.

23  
24 The optimum rate of release of silver ions into an  
25 aqueous environment may be selected by circumstances  
26 and particularly by the specific function of the  
27 released silver. The invention provides a means of  
28 delivering silver ions to an aqueous medium at a rate  
29 which will maintain a concentration of silver ions in  
30 said aqueous medium of not less than 0.01 parts per  
31 million and not greater than 10 parts per million. In  
32 some cases, the required rate of release may be such  
33 that all of the silver added to the system is released  
34 in a short period of hours or days and in other  
35 applications it may be that the total silver be  
36 released slowly at a substantially uniform rate over a

1 period extending to months or even years. In  
2 particular cases there may be additional requirements,  
3 for example it may be desirable that no residue remains  
4 after the source of the silver ions is exhausted or, in  
5 other cases, where the silver is made available it will  
6 be desirable that any materials, other than the silver  
7 itself, which are simultaneously released should be  
8 physiologically harmless. In yet other cases, it may  
9 be necessary to ensure that the pH of the resulting  
10 solution does not fall outside defined limits.

11  
12 Generally, the mole percentage of these additives in  
13 the glass is less than 25%, preferably less than 10%.

14  
15 Embodiments of the invention will be described with  
16 reference to the following non-limiting examples.

17  
18 **Example 1**

19	Component	Mole %
20	Glass Composition	
21	Na <sub>2</sub> O	31.05
22	CaO	16.00
23	Ag <sub>2</sub> O	3.88
24	P <sub>2</sub> O <sub>5</sub>	46.08
25	Na <sub>2</sub> PO <sub>3</sub> F	0.97
26	2Al <sub>2</sub> O <sub>3</sub> .B <sub>2</sub> O <sub>3</sub>	2.00

27  
28 100 grams of the sample was heated to 900°C before  
29 being cooled and pulled at 650°C, at 25 km/hr. Overall  
30 the fibre was good; one sample was 10 km in length and  
31 11 grams in weight, although there was some  
32 crystallisation at the pulling temperature.

33  
34

1     **Example 2**

2	Component	Mole %
3	Glass Composition	
4	Na <sub>2</sub> O	29.51
5	CaO	15.21
6	Ag <sub>2</sub> O	3.68
7	P <sub>2</sub> O <sub>5</sub>	43.80
8	2Al <sub>2</sub> O <sub>3</sub> ·B <sub>2</sub> O <sub>3</sub>	1.90
9	Na <sub>2</sub> PO <sub>3</sub> F	1.90
10	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	1.00
11	Na <sub>2</sub> PO <sub>4</sub>	3.00

12  
13     74 grams of the sample was heated to 1000°C before  
14     being cooled and pulled at 635°C at 25 km/hr. The  
15     fibre produced was ultrafine; one sample was 18 km in  
16     length and 59 grams in weight. The sample was sprayed  
17     with WD40 to prevent water absorption and to aid  
18     lubricity. There was some debris at the bottom of the  
19     crucible, but this was found to be just iron deposits  
20     from the brushing rod.

21  
22     **Example 3**

23	Component	Mole %
24	Glass Composition	
25	Na <sub>2</sub> O	34.20
26	CaO	16.15
27	P <sub>2</sub> O <sub>5</sub>	44.65
28	Na <sub>2</sub> SO <sub>4</sub>	5.00

29  
30  
31     200 grams of the sample was heated to 1050°C before  
32     being cooled and pulled at 635°C at 25 km/hr. The  
33     fibre was good although there was some crystallisation  
34     at the pulling temperature.

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1     **Example 4**

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## 4     Glass Composition

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Component

Mole %

 $\text{Na}_2\text{O}$ 

32.40

 $\text{CaO}$ 

15.30

 $\text{P}_2\text{O}_5$ 

42.30

 $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ 

3.00

 $\text{Na}_2\text{PO}_3\text{F}$ 

1.00

 $\text{Na}_2\text{SO}_4$ 

6.00

12

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19

117 grams of the sample was heated to 950°C before being cooled and pulled at 635°C, at 40 km/hr. The fibre produced was good and there were no crystallisation problems even though the surface temperature of the fibre dropped to 510°C in the pulling process.

20

21

22

**Example 5**

## Glass Composition

23

24

25

26

27

28

29

Component

Mole %

 $\text{Na}_2\text{O}$ 

31.71

 $\text{CaO}$ 

14.73

 $\text{P}_2\text{O}_5$ 

36.33

 $\text{B}_2\text{O}_3$ 

4.78

 $\text{SO}_3$ 

9.40

 $\text{Na}_2\text{PO}_3\text{F}$ 

3.00

30

31

32

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36

99 grams of the sample was heated to 800°C before being cooled to 650°C and pulled at 40 km/hr. The fibre produced was very fine but difficult to pull and quite fragile at speed.

1     **Example 6**

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5     **Glass Composition**

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38

Component

Mole %

Na<sub>2</sub>O

30.77

CaO

14.28

P<sub>2</sub>O<sub>5</sub>

35.28

B<sub>2</sub>O<sub>3</sub>

4.64

SO<sub>3</sub>

9.12

FePO<sub>4</sub>

2.41

W<sub>a</sub>PO<sub>3</sub>F

0.20

Na<sub>2</sub>PO<sub>3</sub>F

0.20

MnHPO<sub>4</sub>

2.06

200 grams of the sample was heated to 850°C before being cooled to 545°C and pulled at 40 km/hr. The fibre produced was strong and thin; there was not a problem of crystallisation, in fact the glass can be stored at 550°C for 72 hours without the onset of crystallisation.

**Example 7**

Below is an example of a wool formulation and running conditions to illustrate the differences with the monofilament examples given above.

A typical wool formulation is

Na<sub>2</sub>O                      26.31

CaO                        17.78

P<sub>2</sub>O<sub>5</sub>                      47.04B<sub>2</sub>O<sub>3</sub>                      5.94

MnO                        1.55

Fe<sub>2</sub>O<sub>3</sub>                    0.97

NaF                        0.41

Solution rate, non annealed = 0.0278 mg.cm<sup>-2</sup>hr<sup>-1</sup>

1 Melted and refined at 1000°C.  
2 Cooled and held at 725°C.  
3 Bushing temperature maintained at 365°C.  
4  
5 Thick fibres approx 1.2mm diameter drawn through pinch  
6 rollers at 2.5 M.mm<sup>-1</sup> from a bushing with 6 x 6.5mm  
7 diameter holes. Fibres jet attenuated to produce a  
8 fine wool 5 -15µm diameter. The wool was sprayed with  
9 silicone oil finish during the attenuation process and  
10 collected on a stainless steel mesh conveyor.  
11 Typically, attenuated wools will have diameters of 5 to  
12 20µm. Monofilament fibres will mostly be 20 to 50µm  
13 diameter.

14  
15 **Example 8**

16	Na <sub>2</sub> O	31.19 mole %
17	K <sub>2</sub> O	9.63 mole %
18	Ag <sub>2</sub> O	2.9 mole %
19	B <sub>2</sub> O <sub>3</sub>	2.74 mole %
20	2NaF	0.66 mole %
21	P <sub>2</sub> O <sub>5</sub>	52.88 mole %

22 Furnace at 710°C - 800°C.

23 Bushing at 450°C - 460°C.

24 4.5mm bushing holes.

25 50km per hour pull rate.

26 Good fibres.

27 Solution rate = 1.68 not annealed 2.28 annealed.

28  
29 **Example 9**

30	Na <sub>2</sub> O	32 mole %
31	K <sub>2</sub> O	10 mole %
32	Ag <sub>2</sub> O	3 mole %
33	P <sub>2</sub> O <sub>5</sub>	55 mole %

34

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- 1 Furnace at 850°C.  
2 Bushing at 530°C.  
3 5mm bushing holes.  
4 55kmph.  
5 Good strong fibres.

6

7 **Example 10**

- 8 Na<sub>2</sub>O 32 mole %  
9 K<sub>2</sub>O 10 mole %  
10 (MgO 4 mole %) - added as an anti-microbial  
11 B<sub>2</sub>O<sub>3</sub> 5 mole %  
12 Ag<sub>2</sub>O 3 mole %  
13 P<sub>2</sub>O<sub>5</sub> 46 mole %  
14  
15 Furnace temperature 650°C - 730°C.  
16 Bushing temperature 410°C - 420°C.  
17 Bushing 5.5mm diameter.  
18 Speed up to 100kmph.  
19 Solution rate 0.7 annealed 1.0 non annealed (mg.cm<sup>-3</sup>.hr<sup>-1</sup>).  
20 Very good strong reliable fibre. Very stable.

21

22 **Example 11**

- 23 Na<sub>2</sub>O 36.68 mole %  
24 K<sub>2</sub>O 8.63 mole %  
25 P<sub>2</sub>O<sub>5</sub> 45.09 mole %  
26 B<sub>2</sub>O<sub>3</sub> 5.29 mole %  
27 Ag<sub>2</sub>O 2.59 mole %  
28 (CaO 1.73 mole % to attenuate solution rate!  
29  
30 Furnace temperature 550°C.  
31 Bushing 62 x 5.0mm holes.  
32 Bushing temperature 400°C.  
33 Speed 80kmph.  
34 Very good fibres.  
35 Solution rate 3.11 annealed, 3.8 non annealed (mg.cm<sup>-2</sup>.hr<sup>-1</sup>).  
36  
37 The fibres show excellent tensile strength, flexibility  
38 and shock resistance.

1 The fibres are especially suitable for industrial and  
2 plastics reinforcement controlled release (anti-  
3 microbial, anti-corrosion etc) and rapidly  
4 biodegradable applications.  
5

6 **Example 12**

7 CaO 30 mole %  
8 MgO 20 mole %  
9 P<sub>2</sub>O<sub>5</sub> 50 mole %  
10

11 Furnace at 1050°C.  
12 Bushing 5.5mm holes.  
13 Bushing temperature 700°C - 720°C.  
14 Speed up to 80kmph.  
15 Solution rate TBA.  
16 Very strong fibre.  
17

18 **Example 13**

19 (K<sub>2</sub>O 5 mole %) Trace to alter dissolution rate  
20 CaO 25 mole %  
21 Mg<sub>2</sub>O 20 mole %  
22 P<sub>2</sub>O<sub>5</sub> 50 mole %  
23

24 Furnace 1000°C.  
25 Bushing 5.5mm.  
26 Bushing temperature 560°C - 620°C.  
27 Speed up to 70kmph.  
28 Solution rate TBA.  
29 Very strong fibre.  
30 Anti-microbial.  
31

32 **Example 14**

33 CaO 28.5 mole %  
34 MgO 18.5 mole %  
35 Ag<sub>2</sub>O 3 mole %  
36 P<sub>2</sub>O<sub>5</sub> 50 mole %  
37  
38

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- 1 Furnace temperature 1050°C - 1150°C.  
2 Bushing 4 x 5.5mm.  
3 Bushing temperature 700°C.  
4 Speed 50kmph.  
5 Solution rate TBA.  
6 Very good, strong fibre.  
7 Anti-microbial.

8

9 **Example 15**

- 10 CaO 30 mole %  
11 MgO 20 mole %  
12 P<sub>2</sub>O<sub>5</sub> 50 mole %

13

- 14 As Example 14 (without silver)

15

- 16 The fibres show excellent tensile strength, flexibility  
17 and shock resistance. These fibres are suitable for  
18 applications requiring slower release and greater  
19 tensile strength plus biodegradability. The fibres are  
20 suitable for orthopaedic implants and tissue  
21 engineering applications.

22

23

24

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1     **Claims**

- 2
- 3     1.    A method for forming water-soluble glass fibres,  
4           the method comprising providing a composition  
5           suitable for producing a water-soluble glass and  
6           heating said composition above the melting point  
7           of said glass to form a molten glass, cooling at  
8           least a portion of said molten glass to a pre-  
9           selected working temperature and then processing  
10          said molten glass having said working temperature  
11          into fibres.
- 12
- 13    2.    A method as claimed in Claim 1 wherein said  
14          portion of said molten glass is cooled slowly to  
15          said working temperature.
- 16
- 17    3.    A method as claimed in either one of Claims 1 and  
18          2 wherein said working temperature is 50-300°C  
19          above the T<sub>g</sub> of the glass.
- 20
- 21    4.    A method as claimed in either one of Claims 1 and  
22          2 wherein said working temperature is at least  
23          200°C below the temperature to which the glass is  
24          initially heated.
- 25
- 26    5.    A method as claimed in any one of Claims 1 to 4  
27          wherein glass wool is formed.
- 28
- 29    6.    A method as claimed in any one of Claims 1 to 5  
30          wherein phosphorous pentoxide is used as the glass  
31          former.
- 32
- 33    7.    A method as claimed in any one of Claim 6 wherein  
34          boron containing compounds are used as glass  
35          modifiers.
- 36
- 37    8.    A method as claimed in Claim 7 wherein B<sub>2</sub>O<sub>3</sub> is used  
38          as a glass modifier at a mole percentage of 15% or

1           less.

2

3       9.    A method as claimed in any one of Claims 1 to 8  
4           wherein said glass is a silver-ion releasing  
5           glass.

6

7       10.   A method as claimed in Claim 9 wherein silver  
8           orthophosphate is added during manufacture of the  
9           glass as a source of silver ions.

10

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0443460

United States Patent Application  
COMBINED DECLARATION AND POWER OF ATTORNEY

Attorney's Docket Number 1066-99

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

"Method of Producing Water-Soluble Glass Fibres"

the specification of which:

[c] was filed as a PCT international application Number PCT/GB98/01597 on 1 June 1998.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below, and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter and having a filing date before that of the application(s) of which priority is claimed:

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED Yes/No
United Kingdom	9711178.5	31 May 1997	Yes

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signature of First Inventor

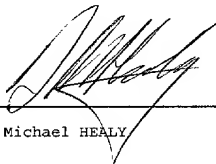


Date

15 November 1999

Thomas GILCHRIST

Signature of Second Inventor



Date

1st November 1999

David Michael HEALY